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Section H

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MONTHLY HEALTH REPORT ON PROBLEMS RELATING TO PRODUCT

For Period Ending November 30, 1944

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Per Letter Instructions Of

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NT Bray

For: M. T. Bray, Supervisor

Laboratory Records Dept.

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## ABSTRACTS

Medical Industrial Hazards Section

220 surveys for product in air were done in New Chemistry. The tolerance ( $5 \times 10^{-10}$   $\mu\text{g/cc}$ ) value was not exceeded. The level of product contamination on equipment has been low. Product contamination in West Stands and Site B Annex has not been high. 4 spills involving product occurred during the month. All have been satisfactorily cleaned up. Personnel surveys are limited by lack of equipment at present.

125 urine specimens from project personnel were analyzed in duplicate for product. No sample gave a significant reading. Urine from a rabbit injected with 20  $\mu\text{g}$  of product was analyzed. The level of activity excreted falls off rapidly after the first few days.

Preliminary work with IR-4 resin as a means of extracting product from urine with little or no pretreatment is encouraging. Further investigation of the IR-1 resin shows some irregularities in the amount of added product which is recoverable.

By altering the method of adding  $\text{BiPO}_4$  and increasing the digestion time, the recovery of product from small amounts (up to 40 cc) of urine has been increased to 90%. Lanthanum fluoride precipitation is the procedure of choice for the analysis of product in urine where the activity per cc is great enough to permit using small volumes (40 cc). The Zirconium phosphate-Lanthanum fluoride method has given good results also when used on samples of high specific activity.

The liquid-liquid extraction methods investigated to date have not been promising. These are the methyl isobutyl ketone and the butyl phosphate systems.

Preliminary work on methods for product extraction from stools will begin next month.

U. of C. Radiation Laboratory

The long term tracer and radio-autographic studies with  $\text{PuO}_2$  smokes are being continued. It is anticipated that in another six weeks a sufficient number of experiments will have been completed so as to permit the presentation of a fairly complete report upon this phase of the tracer problem with product. A new type of smoke generator has been completed which will allow large groups of animals to be exposed and thus improve the relative reliability of results of experiments of this character.

Biological Research Section

K. S. Cole, Section Chief

A. PRODUCT EXPERIMENTS.

1. Development of Aerosol Exposure Methods. 244 MLH 2101

Ether "bomb". As an alternative to using organic complexes in freon it should be possible to use Pu + 6 in dimethyl ether for the "bomb" method of dispersing aerosols. This has the advantage of not introducing extraneous organic impurities although it may introduce an explosion hazard. Preliminary tests indicate that Pu + 6 is as soluble in dimethyl ether as it is in diethyl ether.

2. Preparation of Materials for Aerosol Exposure and Analytical Methods. 244 MLH 2102

Product complexes. The cupferride and oxine complexes of Pu, which have been found to be insoluble in freon "12", have now been demonstrated as soluble in "F-21" ( $\text{CHFCF}_2$ ) and "F-22" ( $\text{CHF}_2\text{Cl}$ ) which are closer approximations to chloroform than the other freons tests. "F-22" is more suitable for "bomb" operation because of its lower boiling point ( $-41^\circ\text{C}$ ). The "bomb" disperses Pu cupferride quite well in either of these solvents, but in all our tests to date the activity has impinged out on the wall of the chamber (a large piece of pyrex pipe of 5 l volume and 2 inches radius). Experiments are under way to solve this difficulty.

Product analysis. Slight changes have been made in our zirconium phosphate method which makes it possible to use samples containing 3 gm bone ash and get the activity on a platinum disc with less than 1 mg of solids. Larger volumes of ash solution are used with a decrease in the relative amount of Zr.

s. The Acute Toxicity of Product in Mice and Rats. 246 MLH 2230a

ABC, brown, male mice and CFl, white, female mice were injected via the tail vein with product in the + 6 state. They received 0.1 to 0.25 ml of the active solution, adjusted to a pH of 2 and made isotonic with sodium chloride. Groups of five or six mice each of both strains received 5, 10, 25, 50, 100, or 200  $\mu\text{g}$  per mouse (0.25 - 10  $\mu\text{g}/\text{gm}/\text{gm}$ . Average weight of mice was 20 grams, therefore, doses in  $\mu\text{g}/\text{gm}/\text{gm}$  body weight were of approximately 0.25, 0.5, 1.25, 2.5, 5 and 10). The white mice which received 200  $\mu\text{g}$  of product each went into shock which lasted for about 15 minutes. At the same dose level the brown mice remained on their feet but were much less active for five to ten minutes following the injections. No untoward reactions followed the injection of 100  $\mu\text{g}$  or less.

All the animals which received 50  $\mu\text{g}$  or more died within the three weeks of the experiment and all but one of each strain at the 25  $\mu\text{g}$  dose level have also died, one white mouse, receiving 10  $\mu\text{g}$ , died on the eighth day, but all the other mice, brown and white strains, at this level and at 5  $\mu\text{g}$ , are alive and appear well and active. The CFl mice were somewhat less resistant to product than were the ABC male mice used in that they died earlier.

Eight mice of a previous experiment which had received 3.6  $\mu$ g (0.18  $\mu$ g/gm), intracardially are alive and apparently well after five months. The six mice which were injected with 36  $\mu$ g (1.8  $\mu$ g/gm) at the same time had died in the first month.

Three rats injected with 55  $\mu$ g (ca 0.25  $\mu$ g/gm of body weight) are also alive after five months. Another series of rats have just been started. Five to ten rats per group were given 0.03 to 2.0  $\mu$ gms Pu/gm of body weight by tail vein injection. No deaths have yet occurred at 9 days although the animals in the 1.0 and 2.0  $\mu$ g/gm groups are losing weight and are inactive and "jumpy". In two animals of 2.0  $\mu$ g/gm group (ca 400  $\mu$ g/rat), the non-protein nitrogen content of their blood plasma rose from 42 and 40  $\mu$ gm N percent before treatment of 197 and 199  $\mu$ gm N percent respectively, four days after injection.

#### 4. Acute Effects of Product on the Peripheral Blood of Mammals. 246 MLH 2440

Mice; No appreciable effect was apparent in the hemoglobin content, erythrocyte, and total leucocyte counts, or in the constituents of the differential blood smears of mice given 0.018  $\mu$ g/gm of product incardially. Likewise, no effect was noted on the erythrocyte or hemoglobin level with 0.18  $\mu$ g/gm. On the other hand a marked fall was noted in the total leucocyte count in the animals injected with .13  $\mu$ g/gm and 1.8  $\mu$ g/gm; this was due to the fall of the total number of lymphocytes and heterophils. After the initial marked fall noted at 4 days, a further decline occurred and death precluded sampling beyond 14 days in the 1.8  $\mu$ g/gm series while a slower decline occurred after 7 days and was still apparent at 84 days in the 0.18  $\mu$ g/gm series.

Rats: Rats receiving product intracardially at 0.25 - 0.28  $\mu$ g/gm show a decline in the total leucocytes, lymphocytes and heterophils to about half the original level by 3 days. A return to normal limits had occurred in the heterophils by 62 days while the total leucocytes and lymphocytes remain approximately at this depressed level throughout 105 days (last sampling).

#### 5. Chronic Toxicity of Product, Injection. 246 MLH 2740a

Intravenous Pu (1 microgram per gram of body weight) produced in CF1 mice within a month, anemia associated with leucopenia and atrophy of the spleen and lymphatic system.

### B. RADIUM EXPERIMENTS.

#### 1. The Acute Toxicity of injected radium in Mice. 363 MLH 2250

As in the product studies, six ABC, brown, male and six CF1, white, female mice were used at each of the following dose levels 1, 2, 5, 10, 20, and 40  $\mu$ c per mouse (0.05 to 2.0  $\mu$ c of radium per gm of body weight). On the 20th day after the intraperitoneal injections it appears that 1  $\mu$ c per gm is fatal to mice, but 0.5  $\mu$ c/gm per mouse is not. The deaths are scattered both below and above these levels. Again the CF1 mice appear to be definitely but slightly less resistant to the toxic agent in the acute stages than are the ABC brown mice. Mice which received radium at .165  $\mu$ c/gm five months ago are now dying. Seven of the original ten are alive, but will probably not survive much longer.

Groups of six ABC mice were given 125, 25, and 5  $\mu$ gms of barium ion per gm of body weight, intraperitoneally. All of the mice of the 125  $\mu$ g/gm group and four of the 25  $\mu$ g/gm group died within twenty-four hours. The 5  $\mu$ g/gm group of mice is intact except for histological sampling and appear to be in good health. The acute lethal dose of barium appears to be the same for the mouse and for man (ca  $\mu$ g/gm of body weight). Because radium is below barium in Group II of the Periodic Table, it can be reasoned that it would be more toxic as an acute chemical poison, but qualitatively similar in action. None of the radium-injected mice were killed rapidly, but usually lasted for ten or more days. Therefore, it is unlikely that radium is chemically more than 10 times as toxic as barium.

## 2. Acute Effects of Radium on the Peripheral Blood of Mammals. 363 MLH 2452

**Mice:** A slight fall in the erythrocyte and hemoglobin level occurred by 123 days in mice given radium intraperitoneally at .165  $\mu$ c/gm. The total number of leucocytes, lymphocytes and heterophils were rather markedly reduced by 4 and 7 days after doses of .165  $\mu$ c/gm and .85  $\mu$ c/gm. These constituents remained moderately reduced through 125 days (last sampling) in animals who received .165  $\mu$ c/gm; death precluded sampling beyond 42 days in animals receiving .85  $\mu$ c/gm.

**Rats:** After an injection (IP) of .165  $\mu$ c/gm of radium as chloride rats showed a fall in the total leucocytes, lymphocytes and heterophils. The depression of the number of lymphocytes was maintained through 125 days while the number of heterophils tended to return slowly toward normal after the initial depression.

## II. Medical Industrial Hazard Section

J. J. Nickson, Section Chief

### Building and equipment surveys for alpha radiation (241 MLH 3300)

#### I. New Chemistry

a) Air surveys for product. 220 surveys were done during the past month. In no instance was the value of  $5 \times 10^{-10}$   $\mu\text{g/cc}$  exceeded (tolerance).

b) Room surveys. All rooms in New Chemistry were surveyed at least once each week. 2 spills were reported. Clean up was satisfactory. The system of reporting unsatisfactory incidents directly to the group leader at the time of discovery was instituted last month. A resurvey is made within 48 hours as a check. Under this system, the number of persistent unsatisfactory incidents has diminished sharply.

#### II. Site B Annex

a) Air surveys. Air sampling for product, radium and radon has been done by this section and by members of the Biology Section. Samples of air have also been submitted to an associated project for radon analysis. In no case have readings indicating greater than tolerance concentrations been obtained.

b) Room surveys. Surveys of the rooms in the building are done at least weekly, or more frequently if alpha activity is handled in them. Several product experiments were carried out during the past month. No instance of other than very minor contamination was noted.

#### III. West Stands

a) Room surveys. The shortage of plutons has limited the frequency of surveys for alpha contamination in this area up to the present time. 2 spills involving product occurred in this area during the past month. One was in room 26, the other in room 212. In both instances the concrete floor was contaminated. It proved very difficult to remove the activity. Because of this, recommendations have been made for the laying of protective, easily removable, impervious flooring in rooms where activities are routinely handled or stored. This recommendation will result in approximately 20 rooms in the West Stands and New Chemistry being so altered.

### Personnel Alpha Surveys (241 MLH 3340)

#### I. New Chemistry

Alpha hand counts continue to be done on a limited scale. Lack of satisfactory equipment is the major factor in limiting personnel surveys. The instrument group is at present designing a number of different types of alpha counters which should resolve this difficulty.

#### II. Site B. Annex

The conditions are as stated under Personnel Surveys, New Chemistry. When instruments are available, this phase of the program can be successfully carried out.

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### III. West Stands

Hand surveys for the personnel from West Stands are at present done in New Chemistry because of the lack of suitable equipment.

Clinical Laboratory for Product Detection (249 MLH 2501) -- Russel, et al.

During the period Oct. 23 - Nov. 20, 1944, 238 analyses were done on 125 individual specimens. No specimens were found to have greater than background counts. (Ten persons, 5 from Site B annex and 5 from West Stands Semi-works submitted daily morning urine samples for a period of 10 consecutive days)

IR-I resin adsorption technique is used for the routine work. The routine work was moved from 210 West Stands to D-7, New Chemistry on October 7, 1944.

Development of methods for detection of product in urine (249 MLH 3502)

#### A. Animal investigations

These investigations are being carried out primarily to provide experience in handling urine with detectable amounts of product. Techniques can be tested easily and rapidly in this way. Excretion curves can be established in experimental animals also.

Rabbit urine from a rabbit injected with 20 mg of product was followed for a period of 100 days. The urine was supplied by the Biological Section of the Health Division. There was no standard procedure for the collection and storage of the urine. The samples were analyzed 4 to 6 months after collection. Under these conditions the results obtained may not represent an idealized picture. However, the information gained may be useful in planning future experiments.

The results of the analyses are given in Figure 1. It is quite clear that there is a very rapid decrease in the amount excreted in the urine but that even after 100 days there are still measurable quantities present.

The discontinuity of the curve cannot be explained at this time since these are the results of only one experiment. It is unlikely that the analyses are in error since both portions of the curve are uniform.

The urine was ashed, the residue taken up in acid and a Zirconium phosphate - Lanthanum fluoride precipitate was mounted on a platinum disc for counting.

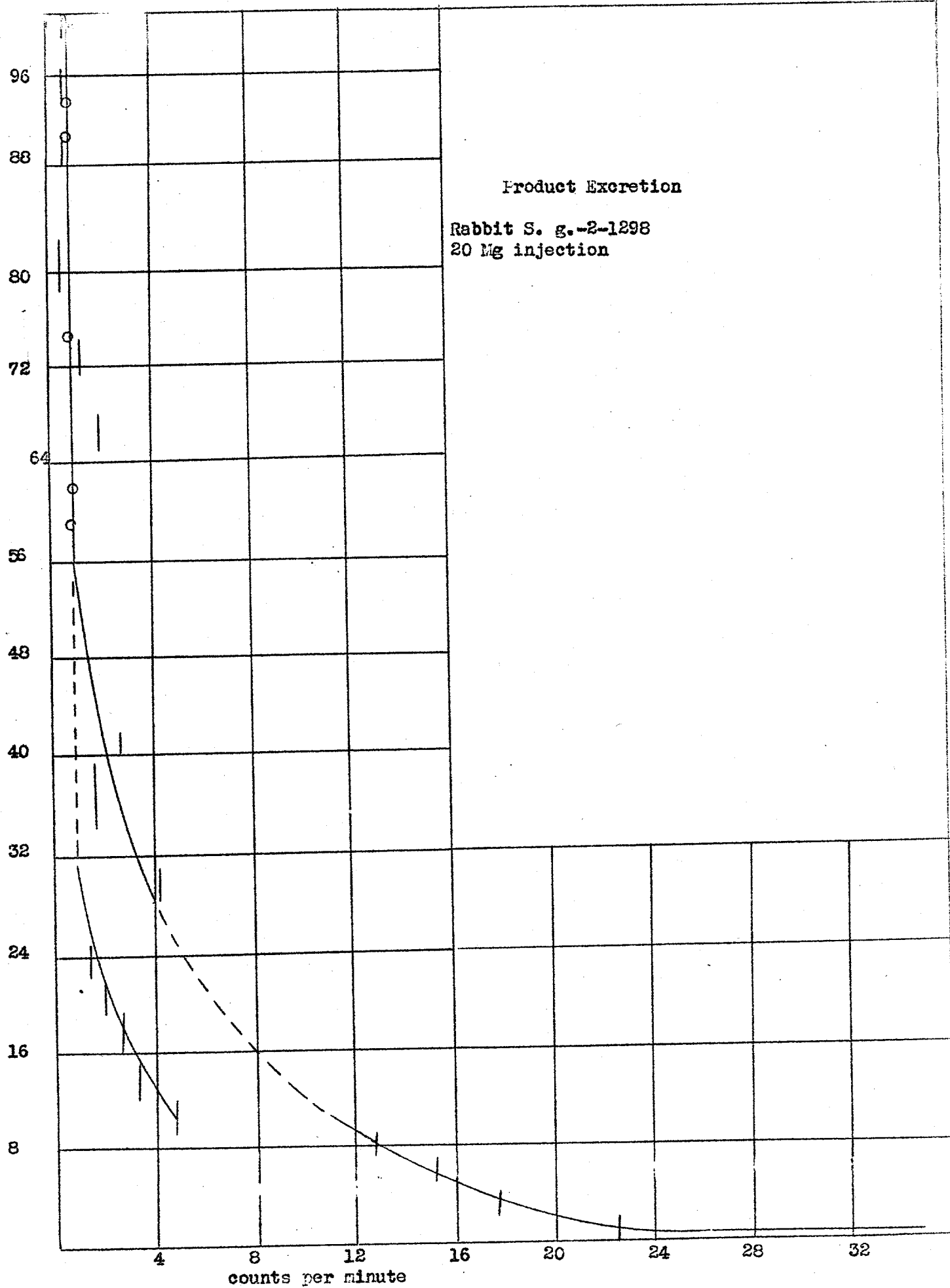
It was reported last month that the naturally occurring precipitate in rabbit's urine carried 90% of the product in the urine. Investigations to determine the composition of that precipitate are now going on. It may be that further knowledge on this point may permit the development of a simple product extraction process applicable to human urine.

#### B. Study of various methods for the extraction of Product from urine.

##### 1. Adsorption methods

###### a) IR-4 Resin

In order that one may rapidly establish certain conditions which will affect the adsorption of product, it is necessary to resort to equilibrium adsorption





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tests. . Any variable which will reduce the equilibrium adsorption will also tend to reduce the adsorption when the column procedure is applied. If an adsorbent will extract a very high per cent of the product in a "batch" experiment, that is, by shaking a given weight of the adsorbent with a specified volume of solution until equilibrium is reached, under similar conditions a column procedure should result in an even higher percentage of extraction.

Previous experience has shown that the amberlite resin IR-4, which is an anion exchange resing, has a very great affinity for the oxalate complex of plutonium. Some batch tests were made in the hope that IR-4 might be a means of removing excreted product from large volumes of urine. In the course of these tests it was found that the resin IR-4 was able to take up product from urine even when no oxalic acid was added.

The general procedure was to add 1 or 2 grams of the resin to 200 ml of urine containing product and shake this mixture for approximately one hour. In some cases oxalic acid was added to the urine and it was then necessary to acidify and dilute to prevent precipitation. After shaking, the urine was decanted and the resin washed with distilled water into a medium fritted glass funnel. Complete removal of the product from the resin was obtained by allowing 6N HCl to percolate slowly through the fritted glass. Since the acid dissolved some of the resin it was not advisable to evaporate and count directly, however, the volume is sufficiently small, 15 ml, for a direct lanthanum fluoride precipitation.

The results of several batch experiments are given in Table II. It is seen that the extraction is fairly satisfactory and that even under these conditions greater than 80% recovery from 1 liter of urine would be more reliable than 95% recovery from 100 ml of solution especially when very low activities are encountered.

The values given in the last column in Table II have not been corrected for losses due to the lanthanum fluoride precipitation. This, however, is not a very important factor.

In the cases where large volumes of urine were used (1000 ml) it may require longer shaking periods for equilibrium to be reached. 5 grams of resin should be used.

During the next month some time will be devoted to further development of this procedure since it does offer some promise as a routine procedure.

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Table II - Batch Experiments on IR-4 Resin

Sample Volume	Weight of Resin	Added Reagents	Shaking Time	% Plutonium Extracted
Spiked Urine (200 ml)	1 gram	none	60 min.	78%
Spiked Urine (100 ml)	1 gram	100 ml 0.8 M oxalic acid	60 min.	74%
Spiked Urine (100 ml)	1 gram	100 ml 0.8 M oxalic acid and 1 M acetic acid	60 min.	81%
Spiked Urine (400 ml)	2 grams	none	60 min.	82%
Spiked Urine (400 ml)	2 grams	none	60 min.	83%
Spiked Urine (800 ml)	3 grams	none	60 min.	70%
Spiked Urine (1000 ml)	4 grams	none	60 min.	68%
Spiked Urine (1000 ml)	5 grams	none	60 min.	68%

Conclusions from the Preliminary Work on the Use of IR-4

(1) In both column and batch work the IR-4 is so changed in its appearance and physical properties, that it is very improbable that it can be used again. The changes are brought about almost entirely by the 6N HCl elutriant. The resin is not expensive.

(2) 15 ml of 6N HCl is sufficient to remove Pu completely from the IR-4 under the following conditions:

- If not more than 6 gm of resin is used.
- If the resin is sucked dry. (After washing with distilled water).
- If a 4 cm M fritted glass filter funnel is used without suction, i.e., the 6N HCl percolates through the resin.

(3) It is better to use a  $\text{LaF}_3$  precipitate from the 6N HCl solution that to evaporate it directly for analysis. A rather large amount of the IR-4 resin

dissolves in the acid and leaves a carbon deposit on the platinum disc which cannot be removed easily.

Addition of some  $\text{HNO}_3$  to the 6N HCl elutriant before diluting decomposes any dissolved resin and helps prevent product losses. This will be tested further.

(4) Two 400 ml batch runs have indicated product yields of better than 80%

(5) If urine is to be run through an IR-4 column, the resin particles should not be smaller than 30-45 mesh.

b) IR-1 Resin

A run was made on a spiked urine sample in order to determine the efficiency of the adsorption method as used at present for routine analyses of urine for product. The equipment and procedure employed was similar to that used in the routine analyses. However, a few variations were introduced.

Four columns were used containing 2.5 grams resin each- instead of 3 grams as in routine analyses. The samples contained 110 cc urine, 10 cc acetic acid, 50 ml  $\text{H}_2\text{O}$ , and 0.2 ml of "spike" solution. Each sample was spiked independently. The rate at which samples were allowed to run was fairly constant - about 1 cc/minute. All solutions employed were saved and analyzed in the hope that most of the product could be accounted for.

The product elutriant and the residue wash were analyzed by evaporation and transfer, while the 0.6 N wash solution and the urine effluent were analyzed by Zr-La precipitation procedure because of the solids they contained.

The results were not too consistent - as shown by the following table.

Product elutriant and 6N wash solution (residue wash) were determined by evaporation and transferring. The 0.6N wash solution and the urine effluent were determined by using the Zr-La precipitation procedure. For the latter procedure 60% carry was assumed and corrections made.

Sample		C/1 min.	Based on 897 c/m = 100%	Corrected for Zr-La ppt'n
#1	Product elutriant	627	69.9	69.9
	Urine effluent	43.2	4.8	8.0
	0.6N wash solution	19.6	2.1	3.5
	Residue wash	39.4	4.4	4.4
	% Product found			<u>85.8 %</u>
#2	Product elutriant	711	79.3	79.3
	Urine effluent	29	3.2	5.3
	0.6N Wash solution	15	1.7	2.8
	Residue wash	29.6	3.3	3.3
	% Product found			<u>90.7 %</u>
#3	Product elutriant	789	88.0	88.0
	Urine effluent	24.5	2.7	4.5
	0.6N Wash solution	12	1.3	2.2
	Residue wash	74	8.3	8.3
	% Product found			<u>103.0 %</u>
#4	Product elutriant	625	69.8	69.8
	Urine effluent	25	2.8	4.7
	0.6N wash solution	20.6	2.3	3.8
	Residue wash	30	3.3	3.3
	% Product found			<u>8.16 %</u>

The percent of product is based on an average of 3 different direct transfers of 0.2 ml of spike solution to disc. The average count/mic was 897.

From this set of experiments it is probably safe to say that the percent recovery is greater than 70%. Since the weight of resins was decreased we should expect no more than 75 to 80% recovery. Less than 5% of the product was found in any of the other solutions.

The variation in the per cent of product recovered may be due to the non-homogeneity of the spike solution used.

During the following month a very critical study will be made on this procedure with the hope of establishing a very definite procedure.

## 2. Extraction Methods

### A) Bismuth Phosphate

As indicated in the last monthly report, the Hanford flowsheet has been adapted to the analysis of urine for product. The procedure indicated in that report has been modified in two ways. The method of adding the phosphoric acid has been changed and the digestion time of the  $\text{BiPO}_4$  has been increased. Both of these changes have increased the recovery of product. The amount of lanthanum used in the lanthanum fluoride precipitation has been kept at 1.5 mg, in order to cut down self-absorption in the final sample. The new procedure is given below.

- (1) To 40 ml of urine add 1.27 ml of 93%  $\text{H}_2\text{SO}_4$ .
- (2) Add 0.416 ml of a 24%  $\text{BiONO}_3$ -19%  $\text{HNO}_3$  solution.
- (3) Raise the temperature of the solution to 75° C. Add 0.1 ml of a 73.5%  $\text{H}_3\text{PO}_4$ -1.2%  $\text{HNO}_3$  solution. Use continuous stirring. Now add 0.05 ml (1 drop) of the Bi solution used in 2.

Complete the precipitation of  $\text{BiPO}_4$  by adding slowly 2.7 ml of the 73.5%  $\text{H}_3\text{PO}_4$ -1.2%  $\text{HNO}_3$  solution.

- (4) Digest the  $\text{BiPO}_4$  for 45 minutes at 75° C. Cool and centrifuge
- (5) Dissolve the centrifuges  $\text{BiPO}_4$  in at least 4 ml of 2N HCl and add 1.5 mg of  $\text{La}^{+++}$
- (6) Make 1N in HF with stirring and let stand five minutes.
- (7) Centrifuge, transfer solid to Pt disc and count.

#### 1. Effect of Phosphoric acid Addition

Previous work indicated a 60-70% recovery of product with the  $\text{BiPO}_4$  method then used. In a routine procedure it had been considered very inconvenient to add the  $\text{H}_3\text{PO}_4$ - $\text{HNO}_3$  dropwise to the urine-Bismuth solution. Therefore, the  $\text{H}_3\text{PO}_4$  was added over a period of only one or two minutes. However, a partial precipitation of the Bismuth in the urine, followed later by complete precipitation, would amount to having two  $\text{BiPO}_4$  precipitates. This might increase the yields. The runs below indicated a 10% increase in our recovery, thus raising the yield to over 80%. In these runs we used the short digestion period of one or two minutes as had been done before. Spiked urine was used. The exact procedure used is given above in part 3 of the new procedure.

<u>Sample</u>	<u>Sample Volume</u>	<u>c/m Added</u>	<u>Time of Digestion</u>	<u>c/m Found</u>	<u>% Recovery</u>
Urine	40 ml	960	2 min.	766	80
Urine	"	"	"	806	84
Water (Control)	"	"	"	845	88
Water (Control)	"	"	"	861	90

## 2. Effect of Digestion Time of the Bismuth Phosphate

In these runs we used the new method of adding the  $H_3PO_4$ . Spiked urine samples were used. Instead of cooling the mixture after the  $BiPO_4$  was precipitated from the urine, the mixture was allowed to digest for 45 minutes at  $750^\circ C$ . The following results indicate that the longer digestion increased the yield.

<u>Sample</u>	<u>Sample Volume</u>	<u>c/m Added</u>	<u>Digestion Time</u>	<u>c/m Found</u>	<u>% Recovery</u>
Urine	40 ml	960	45 min.	840	87
Urine	"	"	"	837	87
Water (Control)	"	"	"	846	88

It is apparent that this modified  $BiPO_4$  procedure, for determining product in urine, gives results comparable to those obtained by using distilled water instead of urine. The present procedure, then, is fairly feasible. The analysis of eight samples, carried through simultaneously, requires about 6 hours work for one person. This is true only if small volumes of urine are analysed. Here the entire analysis is conveniently carried out in a pyrex centrifuge tube. Volumes of 40 ml have been used up to the present, but 90 ml of urine could be analyzed in larger tubes. With volumes greater than 100 ml additional time would be required for filtering and transferring operations.

### b) Lanthanum Fluoride

Because of its simplicity, the direct lanthanum fluoride method of analysis is one worth testing. The large amount of organic matter, sodium and calcium present in urine complicates the situation, however.

The general procedure was to acidify a spiked sample of urine with HCl, add  $La^{+++}$  and then precipitate lanthanum fluoride by adding conc. HF. The lanthanum was centrifuged out, placed on a platinum disc and dried. The disc was then flamed to remove any organic matter and the sample counted. The runs carried out are listed below.

Table III

Lanthanum Fluoride Analysis of Urine for Product

Sample (Spiked)	Volume	La <sup>+3</sup> Used	HCl Concentration	% Recovery
Urine	40 ml	1.5 mg	0.3 M	61
Urine	"	"	0.3 M	73
Water (Control)	"	"	0.3 M	88
Water (Control)	"	"	0.3 M	91
Urine	"	0.75 mg	1.0 M	90
Urine	"	"	1.0 M	91
Urine	"	"	1.3 M	93

From these experiments it appears that the lanthanum fluoride procedure is by far the best to be used when the activity of the sample is sufficiently high for small volumes to be analyzed.

The pyrex centrifuge tubes were attacked slightly by the sodium fluoride. This tended to increase the deposit on the counting disc resulting in self absorption. However, the results indicated that the self absorption. However, the results indicated that the self absorption was not too critical. Very large losses of product were encountered when attempts were made to use lustroid in place of the pyrex tubes.

c) Zirconium phosphate - Lanthanum fluoride Method

1. Application to Rabbit's urine

A sample of active rabbit's urine was centrifuged to remove solid matter. (Note: this urine was collected in a nitric acid solution to prevent the precipitation of product with the solid matter.) Two 10 ml portions of the sample were taken; one was analyzed directly by the  $Zr_3(PO_4)_4$ -LaF<sub>3</sub> procedure while the other was ashed before the analysis was performed. The results are given below.

<u>Sample</u>	<u>Directly Analyzed</u>	<u>Ashed and Analyzed</u>
Counts	280	284

Assuming maximum efficiency for the  $Zr_3(PO_4)_4$  procedure on the ashed sample, the data indicate that the procedure is as efficient for analyzing actual rabbit's urine as it is for analyzing simple solutions.

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2. Studies designed to improve the efficiency of the  $Zr_3(PO_4)_4-LaF_3$   
Procedure for assaying urine for product

A series of experiments designed to determine the effect of nitric acid concentration on the carrying power of zirconium phosphate has been conducted. Certain variations were encountered which have not been completely explained at present, hence complete data will be given in the next report.

3. Liquid-liquid extraction methods

a) Methyl Isobutyl Ketone

One of the methods for purification of product involved its extraction from a highly salted nitric acid solution into hexone (methyl-isobutyl ketone). The product is subsequently extracted from the hexone into water. Reported yields after three extractions by this procedure are 90% or greater. The procedure, as carried out by the purification group, was applied to a spiked urine sample.

Three experiments were conducted to test the feasibility of extracting product from urine with hexone. Complete data will not be listed since the results were somewhat erratic. No yields greater than 10% were obtained and no simple analytical procedure was perfected for determining the amount of extracted product. In view of the difficulties experienced in developing the techniques in connection with this method, it was deemed inadvisable to pursue it further at the present time.

b) Butyl Phosphate

Butyl phosphate is known to extract product from a salted nitric acid solution. This experiment was designed to test its efficiency for extracting product from urine. Only one simple extraction was performed. The experiment was conducted as follows: A solution of urine with a total volume of 10 ml containing 4 g of  $NH_4NO_3$  + 1.87 ml  $HNO_3$  + 1 ml of stock product solution was shaken for 10 minutes with 10 ml of butyl phosphate. Stock solution contained 600 ac/.1 ml. After separation of the layers, 0.5 ml of each was evaporated and counted for product.

<u>Sample Counts</u>	<u>Urine Phase</u> <u>98/0.5 ml</u>	<u>Butyl Phosphate Phase</u> <u>116/0.5 ml</u>
Counts in phase	1960	2320
% in each phase	32.6 %	38.6 %
Total counts	4280	
Material Balance	71.5 %	

As the data show, butyl phosphate does extract product from urine but the low efficiency for extraction did not warrant further study at this time.

Methods for detection of product in feces (249 MLH 3511)

No work has been done during the past month on this problem. It is planned to devote some time next month to preliminary investigation. Feces obtained from product injected dog will be used.

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Detection of product in feces (249 MLH 3510)

No routine work has been done on this problem as yet. It is not anticipated that routine work on human stools will begin before January, 1945.

Detection of product in sputum (249 MLH 3520)

No routine work is planned at the present time on this problem.

## Associated Projects

IV. CLINTON LABORATORIESHEALTH DIVISIONHEALTH-PHYSICS SECTION OF HEALTH DIVISION

Report by K. Z. Morgan, Section Chief  
and R. H. Firminhac, Group Leader

1. Product Activity of the Air

$5 \times 10^{-10}$   $\mu\text{g/cc}$  is the temporarily accepted tolerance. When readings indicate greater concentration they are called "high", and when lower concentrations "low". Contamination of the air with product was found to be above  $5 \times 10^{-10}$   $\mu\text{g/cc}$  in several areas during the month. None of the high concentrations persisted nor were the causes of all determined. The most noteworthy cases were as follows:

1. Room 54 - Chemistry Bldg.

In this room several readings above  $5 \times 10^{-10}$   $\mu\text{g/cc}$  have been obtained in recent months in front of a particular hood. These cannot be traced to any specific operation in the hood.

2. Room 22 - Chemistry Bldg.

Readings indicating above tolerance levels were found in front of a hood on one day, but the following day when the same operation was carried out, below tolerance levels were found. The only change known to have been made was to allow more air to enter the room, which had been operating under slightly reduced pressure.

3. Product Extraction Bldg.

Over tolerance readings were found for most of one day in front of all hoods. There is some evidence that the hood action was reversed and that air was actually entering the room through the hoods. The situation corrected itself by the next day and the cause is still unknown.

4. Semi-Works

Several high readings were obtained here, but in all cases they were anticipated by the operators, monitoring requested and masks worn. Two high readings were obtained over solutions of moderate product concentration which were being heated, and a third in a Cell where the ventilating system was out of order.

2. Jetting of Solutions

The new system of jetting solutions from the cans (from the Product Extraction Building) to the Room D tank has not caused any serious air contamination to date. However, a very high reading was found in the air at the ventilator outlet on the roof. Pluto surveys revealed no serious contamination on the roof surface. Several improvements have been made in Room D. Stainless steel catch

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pans have been made in order to simplify the procedure of cleaning up contamination and the tops have been welded down on some of the tanks. The room has been cleaned carefully and painted.

### 3. Precipitron vs the Filter Paper

As mentioned in the October Cn-H report both the precipitron and the filter paper method seem to be satisfactory for product dust collection, provided the new type of filter paper is used. Mr. Pfanstiehl of the Metallurgical Laboratory has investigated the procurement of the highly efficient asbestos type paper and finds that it is available in sufficient quantities to meet the need. In view of the fact that this filter paper is as efficient as the precipitron and because of the simplicity of the filter paper method of collection, plans are under way to put the filter paper method of collection to more general use. The procurement of a good blower seems to be the major problem remaining at present.

### 4. The Handie

This is the name selected by Mr. Borkowski for the new cylindrical screen type alpha hand counter which he developed. This instrument is by far the most useful one that has been devised for alpha hand counting and for checking certain kinds of equipment. Two of these instruments are in operation. The geometry of these instruments under operating conditions in the 204 Bldg. is only about 10%. As high as 30% geometry has been observed under ideal counting conditions of a quiet counting room. Several improvements and modifications of this instrument are under way.

### 5. Clothing Decontamination

Mr. H. A. Moulthrop's work on product decontamination of clothing in the laundry indicates that citric acid, when used in a hot 3% solution of pH 5 or less, may prove very satisfactory for removing product contamination. The present indications are that citric acid is just as effective as the acetic acid (now being used) in removing beta and gamma fission activity. The citric acid gave 90% removal of product, whereas the acetic acid gave only 10% removal. A quantity of citric acid is now on order and tests will be made on an operations scale very shortly. The citric acid costs about 20¢ per pound; the acetic acid 8¢ per pound. However, the citric acid may be cheaper in the long run since it would reduce the number of rewashes. In any case, the citric acid would represent a negligible portion of the cost of the operation of the laundry and the added efficiency should be the determining factor. //

Ref: H. A. Moulthrop to K. Z. Morgan 11/18/44  
L. D. Pahnke to K. Z. Morgan 9/29/44

### 6. Product Activity of Discharge Water

Mr. W. Singlevich made a quantitative determination of the product content of the water entering the settling pond. The alpha activity of this water was 0.083 disintegrations per minute per cc or  $5.75 \times 10^{-4}$   $\mu$ g of product per liter of water. If the flow from the settling pond is  $3 \times 10^6$  liters/day, this would carry 1.7 mg of product per day. Of course the product content of

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of the settling pond varies considerably from time to time, and the value of 1.7 mg/day is probably the low figure. One would expect the average value to be about 100 mg/day on the basis of amount lost in extraction. The product activity of the water is not considered comparable from an immediate health hazard point of view to the ~ $\mu$ curies/day of beta and gamma fission activity entering the settling pond. However, if a simpler method of product analysis can be developed, there may be some reason to believe that a more frequent check on the product discharged from the plant would be of more than idle interest.

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